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Structural and electrochemical characterization of $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ as an electrolyte for SOFC-H

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Abstract. As a potential electrolyte for proton-conducting solid oxide fuel cells (SOFC-Hs) and to get better protonic conductivity and stability, zinc doped BCZY material has been found to be promising. In this study, we report a new composition of proton conductors $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ (BCZYZn5) which was investigated using XRD, SEM and conductivity measurements. Rietveld refinement of the XRD data reveal a cubic perovskite structure with Pm-3m space group. $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ shows cell parameter $a = 4.3452(9)$ Å. Scanning electron microscopy images shows that the grain sizes are large and compact which gives the sample high density and good protonic conductivity. The total conductivity in wet atmosphere is significantly higher than that of dry condition and the conductivity was found to be $0.276 \times 10^{-3} \text{ Scm}^{-1}$ and $0.204 \times 10^{-3} \text{ Scm}^{-1}$ at 600°C in wet and dry Ar, respectively. This study indicated that perovskite electrolyte BCZYZn5 is a promising material for the next generation intermediate temperature solid oxide fuel cells (IT-SOFCs).

1. Introduction

These invention of Solid Oxide Fuel cells (SOFC) brings a great advantage in renewable and sustainable energy system for future generation. This is the most efficient device among the energy technology invented so far [1]. In recent years proton conducting electrolytes brings a great advantage in SOFCs technologies to operate in intermediate temperatures. They have a growing interests in proton-conducting oxide electrolytes for SOFCs and a wide range of technological applications in fuel cells, batteries, gas sensors, hydrogenation or dehydrogenation of hydrocarbon electrolyzers [2-4]. A lots of perovskite type oxides show high proton conductivity in H_2 and H_2O containing atmospheres at relatively low operating temperatures ($400\text{--}700^\circ\text{C}$), low activation energy and high efficiency [5, 6]. Finding the best proton conducting and proper compromise perovskite material between conductivity and chemical stability is a great challenge. To get highly densified materials at low sintering temperature



for proton conducting electrolyte is also a major challenges. BaCeO₃-based materials may exhibit mixed ionic (oxide ions and protons) conduction [7, 8]. Doped barium cerates (BaCeO₃) possess high proton conductivity and good sintering behavior [9, 10], though they are unstable in CO₂ and steam, destroying the perovskite structure [11], which is essential to the maintenance of high proton conductivity. On the other hand doped zirconates which offer low proton conductivity and poor sinter ability but high chemical stability in CO₂ and H₂O atmospheres [12-16]. In combining these two doped, an apparent optimized material could be obtained. In recent reports the solid solutions of BaCeO₃ and BaZrO₃ combined the high proton conductivity of barium cerate with the good chemical stability of barium zirconate [17, 18], despite the fact that the sintering temperature was still very high [19]. Recently it was reported that the better chemical stability obtained by partial substitution of Zr⁺⁴ cations into Ce⁺⁴ cations as an electrolyte material [20, 21]. The introduction of small amount of Zn at B-site into the structure allows a reduction in high sintering temperatures and a remarkable improvement in the stability, relative density and conductivity [22]. As a potential high performance proton conductor BCZYZ has been offering the benefits of both stability and increased proton conductivity [23]. These oxides also exhibit mixed proton and oxide-ion conductivity [24] upon exposure to humid atmosphere. This new material for proton conducting electrolyte offers to minimize those challenges.

In this study we report a new proton conducting perovskite series BaCe_{0.7}Zr_{0.2}Y_{0.05}Zn_{0.05}O₃ to overcome those major challenges. We have studied the thermal and electrochemical properties of the series using XRD, SEM and conductivity measurements.

2. Experimental

The zinc doped BCZY powder materials were prepared by using solid state reaction method. Stoichiometric amount of BaCO₃, CeO₂, ZrO₂, Y₂O₃ and ZnO were mixed by ball milling with zirconia balls and acetone to ensure thorough mixing for 24 h. The finely ground dried materials were fired at 1000°C for 8 h with a fixed heating rate of 5°C min⁻¹ and subsequently ground and palletized using 13mm diameter die and Kennedy Hydraulic Bench Press under pressure of 202 MPa (3 ton) and sintered at 1200°C in air for 18 h with a fixed heating rate of 5°C min⁻¹. The final sintering temperature was 1400°C in air for 22 h with a fixed heating rate of 5°C min⁻¹ using Nabertherm box furnace.

The phase structure, purity, identity and homogeneity of the mixed oxide was examined by at ambient temperature using Shimadzu-7000 diffractometer (CuKα₁=1.5406 Å) in the 2θ range from 10° to 80°. The data were collected with a 0.01° step size and a count time of 60 s/step. The obtained data were refined by the Rietveld method using the FullProf software [25]. The microscopic features of the prepared electrolytes were characterized using sub-nanometer resolution Scanning Electron Microscope (JSM-7610F). The SEM data were collected in atmospherically-isolated chamber.

To measure the deformation of the sample materials under non-oscillating stress against time or temperature, with programmed temperature using SETARAM Instrumentation-SETSYS Evolution TMA S60/28682-LCT10414-3. For the BCZYZn5 material, the thermal expansion coefficients properties are measured by thermomechanical analysis. To determine both the size of particles and their state of distribution of BCZYZn5 material, Horiba Particle Size Distribution Analyzer LA-920 and Horiba Reservoir Unit LY-201 were used in wet mode.

The conductivity of the sample was analyzed by using Impedance Spectrometry. A Solartron 1260 frequency response analyzer connected to a ProboStat (NorECs, Norway) conductivity cell was used to measure impedance over the frequency range 6 MHz to 1Hz and the applied sine wave amplitude was 1 V rms. a sintered pellet of the as-prepared material, 13 mm in diameter, and with approximately 0.5 cm² platinum paste electrodes were used. Impedance data were initially collected on cooling from 1000 to 150°C (cooling cycle) in 50°C steps under flowing dry and wet Ar. The gas was passed through two beds of P₂O₅ desiccant before entering the conductivity cell and is called the 'Dry Ar'. Whereas, when Ar gas was flowed through water at 22°C (p(H₂O) = 0.026 atm) and the measurement is called 'Wet Ar'. Each time, sufficient time was allocated at each temperature to ensure equilibrium before spectra was

recorded. The least squares refinement program Z-View (Scribner Associates Inc.) was used to fit the obtained impedance data.

3. Results and discussions

3.1. X-ray Diffraction Analysis

Rietveld refinement of XRD data shows the $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ material as cubic symmetry in the space group Pm-3m. Table 1 shows the unit cell parameter is $a = 4.3452(9)$ Å.

Table 1. Summary of result obtained from Rietveld analysis of X-ray diffraction data for BCZYZn5

Sample	Space Group	Lattice Parameter (Å)			Chi ² (χ^2)
		a	b	c	
$\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$	Pm-3m	4.3452(9)	4.3452(9)	4.3452(9)	1.36

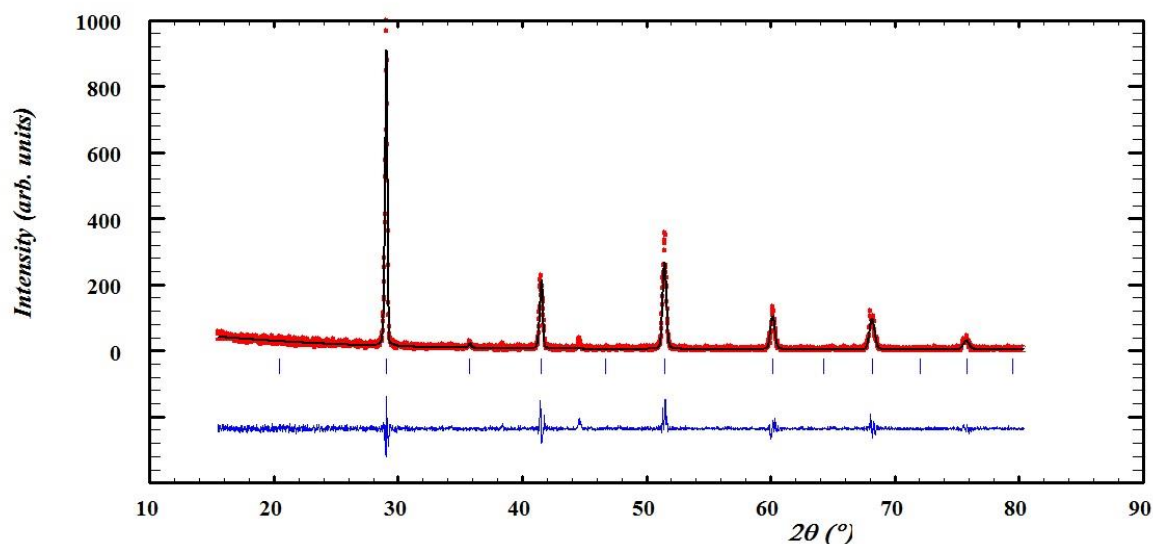


Figure 1. Rietveld analysis of X-ray diffraction data for BCZYZn5 as Cubic.

Figure 1 shows the Rietveld refinement of XRD of BCZYZn5 in cubic symmetry. The refinement converged quickly with significant improvements to the fit achieved when oxygen occupancies were allowed to vary from full occupancy. The occupancies of A and B site components were also checked and found to be fully occupied. The refinement of oxygen sites indicate the overall oxygen contents of O_{2.96} which is very close to the value required to conserve charge neutrality. The B-site occupancies were found as the expected stoichiometry within the limit of standard deviation. Decreasing Zr concentration leads to an increase of the lattice parameters. This increase of parameters reflects the substitution of small Zr⁴⁺ for Y³⁺-site. These results suggest that these compositions could be good approach as electrolyte materials in SOFC-H.

3.2. Scanning Electron Microscope Analysis

To observe the microstructures of the sample series, scanning electron microscopy was applied. Figure 2 a) shows the SEM top-view of surface morphology of the as-prepared BCZYZn5 materials. The surface was smooth and free of cracks. Thus, this compositions indicated non porosity, no trace of liquid or secondary phases were found at the grain boundary region in any of the samples investigated. It also shows that the grain sizes are larger and compact full which gives high density. Figure 2 b) shows the

similar work but sample composition was different [26]. Comparing this two figures that for Figure 2 a), the grain size is much bigger than 2 b). For BCZYZn5 the small spherical phase is approximately 1 μm . The large grain size gives less grain boundary resistance also. The SEM data were collected with a voltage of 5 kV and with magnification of 3000 times. These results suggest that the introducing of Zn leads to a compactness of the grain size.

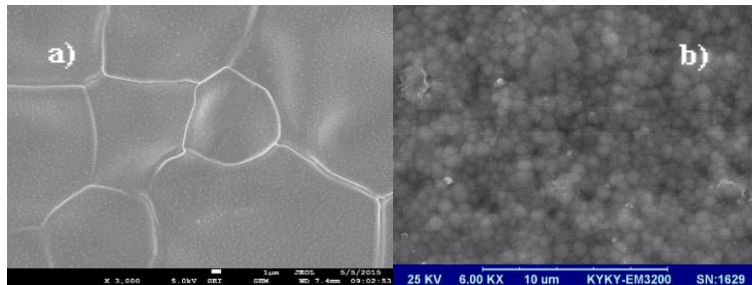


Figure 2. a) SEM analysis of $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$, b) SEM image of $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ [26].

3.3. Thermo-Mechanical Analysis

The result of thermal expansion curves for $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ oxide materials, shows the lowest of all temperature ranges. In Figure 3, the thermal expansion coefficient (TEC) increases with the increase of Yttrium % and also with the temperature. The TEC is also increased with the decrease of Zirconium %. To analyze the thermomechanical properties of the composition, the TEC is $10.919 \times 10^{-6}/^\circ\text{C}$ at 898.92°C .

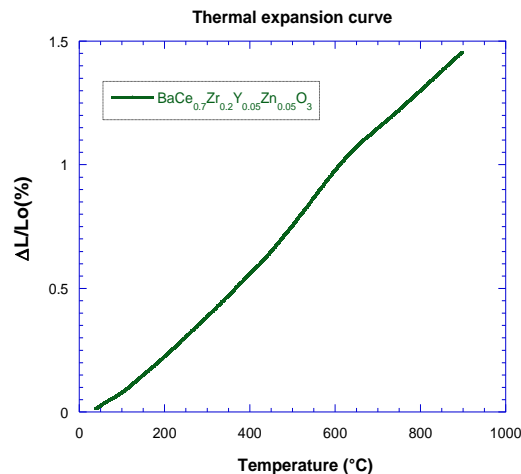


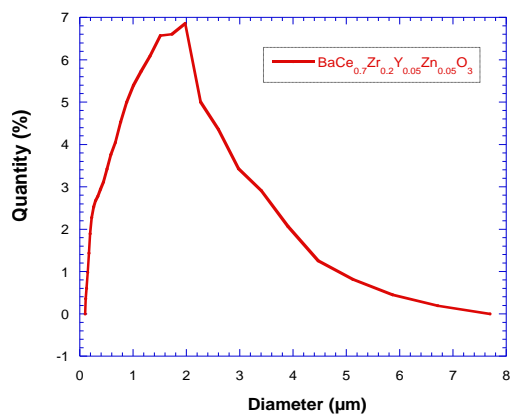
Figure 3. Thermal expansion curve for $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$

3.4. Particle Size Measurement

The particle size distribution for the metal oxides used in this investigation was calculated in powder after sintering at 1400°C . The metal-oxide powders were previously sonicated during 4 h at 60°C to obtain a homogeneous particles dope. Table 2 shows that, as the increase of increasing of Y concentration with Zr leads to a decrease of the particle size. The addition of metal oxide particles not only increases water diffusion into the growing membrane due to its higher hydrophilic nature but also affects the interaction between polymer and solvent molecules by the hindrance effect of the particles. From figure 4 and, it was indicated that the quantity (%) of the sample varies with the diameter of particle size and the diameter range of the BCZYZn5 material remain within 0-2.5 μm .

Table 2. Particle size analysis: with standard deviation

Sample	Quantity (%)	Diameter (μm)	Standard Deviation (S.D)(μm)
$\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$	6.856	1.981	0.9329

**Figure 4.** Quantity vs Diameter curve of $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ for particle size.

3.5. Impedance Spectroscopy

The total and bulk conductivity increases along with the concentration of Y^{3+} dopant. This trivalent dopant creates more vacant oxygen sites and in turn increases the proton concentration. Figure 5 shows the Arrhenius plot of the sample in hydrate (under dry Ar) and as-prepared (under wet Ar) form. The bulk conductivity in wet and dry Ar atmosphere was 0.00136 Scm^{-1} and $0.000946 \text{ Scm}^{-1}$ at 600°C and, $0.004242 \text{ Scm}^{-1}$ and 0.00331 Scm^{-1} at 900°C , respectively. Similarly the total conductivity in wet and dry Ar atmosphere was $0.000276 \text{ Scm}^{-1}$ and $0.000204 \text{ Scm}^{-1}$ at 600°C , and $0.003014 \text{ Scm}^{-1}$ and 0.00218 Scm^{-1} at 900°C respectively. Figure 6 shows that the conductivity increases with temperature as well as wet atmosphere. The increase of total conductivity is smoother than the bulk conductivity. Slodczyk et al. reported that the BCZYZ ceramic – offering an high conductivity and stability as a potential candidate for use as an electrolytic membrane which was suited to the surface and bulk analysis [23]. In the present work, we have got higher conductivity in BCZYZn5 in comparison to BCZYZ reported by Slodczyk et al.

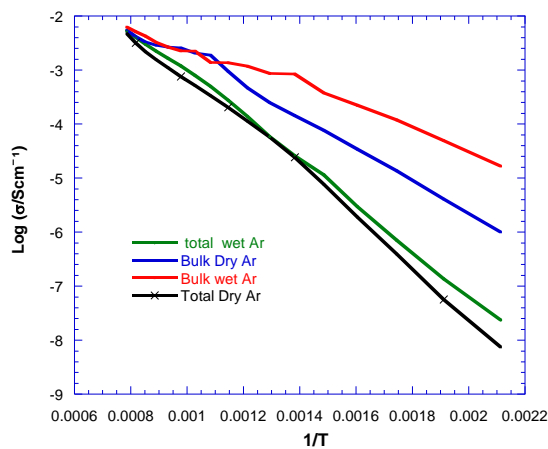


Figure 5. Arrhenius plot of the sample BCZYZn5 in dry and wet Ar. Bulk and total conductivity is also shown.

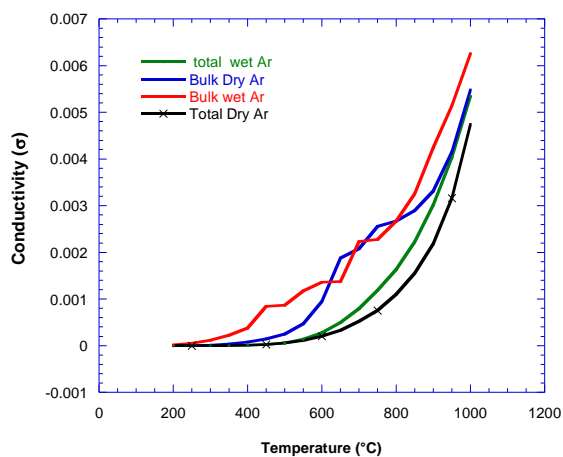


Figure 6. Conductivity vs Temperature of the sample BCZYZn5 in dry and wet Ar. Bulk and total conductivity is also shown.

4. Conclusions

The In this study, $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ proton conducting electrolyte was successfully fabricated. Rietveld analysis of the XRD data indicates that the samples crystallize in cubic symmetry. The SEM analysis shows the electrolyte materials are non-porous and highly dense. The electrical measurements performed in different atmospheres have shown that adding Zn was beneficial in terms of increased conductivity values. For BCZYZn5, Bulk conductivity reaches 1.36×10^{-02} at 600°C in wet condition with an activation energy of 0.58 eV. To get high protonic conductivity and high stability zinc doped BCZYZn5 material has been found to be promising as a potential electrolyte for proton-conducting SOFCs.

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